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The potential, limitations, and challenges of divide and conquer quantum electronic structure calculations on energetic materials

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Abstract

High explosives are an important class of energetic materials used in many weapons applications. Even with modern computers, the simulation of the dynamic chemical reactions and energy release is exceedingly challenging. While the scale of the detonation process may be macroscopic, the dynamic bond breaking responsible for the explosive release of energy is fundamentally quantum mechanical. Thus, any method that does not adequately describe bonding is destined to lack predictive capability on some level. Performing quantum mechanics calculations on systems with more than dozens of atoms is a gargantuan task, and severe approximation schemes must be employed in practical calculations. We have developed and tested a divide and conquer (DnC) scheme to obtain total energies, forces, and harmonic frequencies within semi-empirical quantum mechanics. The method is intended as an approximate but faster solution to the full problem and is possible due to the sparsity of the density matrix in many applications. The resulting total energy calculation scales linearly as the number of subsystems, and the method provides a path-forward to quantum mechanical simulations of millions of atoms.

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Chapter 1

Introduction

High explosives (HE), a class of reactive materials, are used extensively in mining and weapons applications. They are also used in fundamental research as they allow experimenters to achieve pressures and conditions akin to the surface of stars or interiors gas giant planets that are extremely difficult to probe otherwise. Designers and experimentalists demand ever-increasing control and understanding of the detonation process to maximize the safety and accuracy of the applications.

Even today, the fundamental understanding of the detonation process is limited because measuring the details of the detonation region is prohibitively difficult to perform [1]. Computer simulations can be of great value here. It is possible to numerically simulate the motions of atoms on time and length scales of the denotation process (millions of atoms for many picoseconds). Most atomistic simulations of detonation involve the use of empirical force fields describing the interactions between atoms. The advantage of force fields is that simulations involving thousands to millions of atoms can be achieved. However, standard force fields do not describe the chemical bond formation and breaking that is of paramount importance to the explosive energy release. More elaborate force fields such as ReaxFF describing bonding have been created [2, 3] and tested on PETN for example [4]. However, the veracity is in question at the high temperatures of detonation. It is in part a goal of this effort to assess the utility of ReaxFF methods for HE.

Molecular dynamics simulation (MD) is a powerful tool that can be used to examine physical and chemical changes occurring at the atomic scale. Developing predictive models of the initiation of detonation and the sensitivity of high explosives demands the large-scale coupling of both chemistry and physics in the simulations.

Quantum mechanical methods such as traditional quantum chemistry, density functional theory, or semi-empirical methods intrinsically describe bonding and are the fundamental theory to simulate detonation. However, even the most approximate semi-empirical quantum methods are limited in the number of electrons and ions they can describe. This is because of a typical N^3 or worse scaling rule for quantum mechanical eigensolvers, where N is the number of electrons involved. Current state-of-the-art implementations can describe 100s to 1000s of atoms at some level of quantum mechanics simulation. Recent efforts have used *ab initio* quantum MD to study nitromethane [5, 6]. Even in this case, the effort is computationally demanding and many approximations such as the tight-binding one must be used. *Snap-shot* density functional theory (DFT)calculations - instantaneous frozen atomic positions or limited time extend - have been performed on small models of Solid Nitromethane, HMX, RDX, and CL20 [7].

In this SAND Report, we describe the development of a tool to provide quantum mechanical simulations of high explosives that is intended to to be used within the quantum molecular dynamics (MD) formalism. The divide and conquer (DnC) scheme can also be generalized to *ab initio* and first principles quantum chemistry approaches whereby no empirical assumptions beyond the validity of the Schrödinger equation.

The divide and conquer method in quantum chemistry goes back to pioneering efforts by W. Yang to linearize DFT within a local atom centered basis set [8, 9, 10, 11, 12, 13, 14]. He performed a series of tests on polymers obtaining total energies at reduced computational cost. Other authors have developed this work adding more sophisticated buffer regions and extending applicability to other *ab initio* and quantum chemistry methods [15]. Recent large scale efforts have shown promising results [16, 17, 18, 19, 20, 21, 22]. One of the principle challenges when using divide and conquer methods is the selection of subsystems. Several recent attempts focus on using the spatial positions of the atoms to design subsystems. The use of hierarchical real space grids to perform DnC was attempted [23, 24]. A 3D fragment method was also explored [25].

The key idea in divide and conquer is that the diagonalization of the Fock matrix can be approximated efficiently when described in terms of a spatially localized basis set. Diagonalization of the Fock matrix typically scales as N^3 where N is the number of basis functions can be greatly reduced in many situations. The full Fock matrix for a many-atom system with a band gap is sparse in a local atom centered basis set. This is often described in terms of the short-sightedness of the electron-electron interaction. Thus, knowledge of the relative locations of the atoms can be used to reduce the full problem to many smaller sub-problems. With a judicious choice of subproblems, the solutions can be expected to agree reasonably well for total energy, forces on the ions, and harmonic frequencies.

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Chapter 2

Method

The basic idea of the divide and conquer (DnC) algorithm is a partitioning of the density matrix expressed in an atom centered basis into spatially-local blocks and to diagonalize a reduced Hamiltonian in these blocks separately with care taken to match between blocks [8, 9, 10]. The scheme allows the reduction of a the matrix diagonalization problem of order N^3 to much lower order, perhaps even order N for sparse Hamiltonians. This is a vast computational speed-up. The scheme is physically motivated since in many realistic contexts the electronic density is locally determined and can be described through local and semi-local density functional methods, however, certain aspects of long-range charge transfer and interactions can be neglected in DnC. Methods have been developed to extract energy gradients from the Hamiltonian fragments [11], and these gradients are vital to implementing this scheme in molecular-dynamic contexts. This DnC scheme can be generalized to Hartree-Fock in addition to density functional methods thereby opening up a wide array of semi-empirical method that can be used [26]. One of the most challenging parts of this framework is the choice of partitioning schemes, and several recent works have considered efficient ways to partition the many atom systems [25, 24].

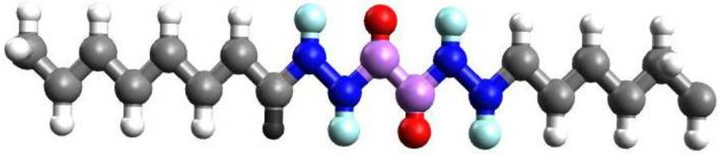

Figure 2.1. Illustration of a fragment and a buffer for simple model of linear polymer. The purple and red atoms are the Carbon and Hydrogen atoms respectively of the fragment. The blue and azure atoms are the Carbons and Hydrogens of the buffer. In a DnC calculation the fragment and buffer regions are explicitly treated as a local problem and solved discretely. Global information feeds back into the calculation through the self-consistency cycle and the construction of the Fock interaction matrix.

We have developed a program that uses the DnC algorithm to perform quantum chemical calculations of energies and forces on macro-molecules and clusters. The divide and conquer scheme takes advantage of sparsity. The DnC algorithm in DFT and quantum chemistry reduces the computational cost of diagonalizing the Fock operator. For a system with N basis functions, this requires N^3 operations. However, the Fock matrix is sparse for many systems of interest such single molecules and oxides, systems with an energy gap in the density of electronic states. For a sparse matrix, many of these operations are on negligibly small contributions. If each of the subproblems is greatly smaller than the total system size, the scheme effectively reduces the required computations to order N. In practice it is convenient to define buffer zones around each fragment that are included in the subsystem calculations but do not contribute fully to the total energy.

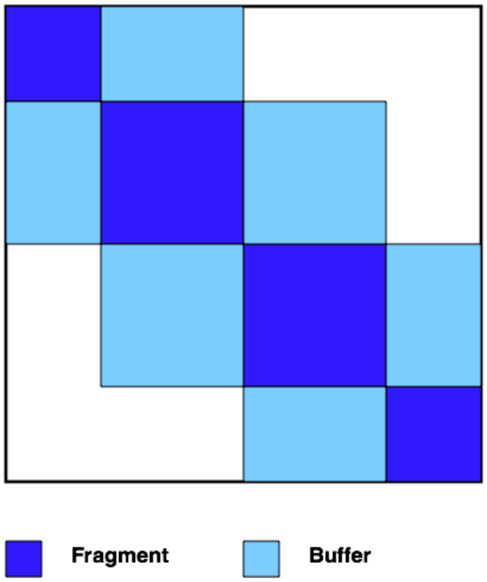

Figure 2.2. Illustration of a partitioned Fock matrix demonstrating that the principal support in a local basis is mostly block diagonal.

We have coded this method in the Python scripting language. For the quantum mechanics solver, we use PyQuante, a python program that is capable of running quantum mechanics simulations within density functional and semi-empirical formalisms. The DnC implementation requires the Python libraries Pypar, Scipy, and Numpy as well as PyQuante's required dependencies. Calculations were performed on TLCC Glory cluster which has 272 compute nodes with 2.2GHz AMD quad socket/quad core processors, 32 GB DDR2 RAM per node and Infiniband with OFED stack interconnect. Parallel DnC calculations of 1000 atom systems were performed using 4-18 nodes (16 cores/node) and required a typical computation time ranged from 24 to 80 hours in real time. For each total energy point, the implementation is parallel in the calculation of the fragment plus buffer systems.

The fragments can be chosen manually by appealing to obvious discrete units such as picking polymer monomers as was done in the earlier implementations. However, a scheme to find the forces for dynamically evolving systems requires automation. An attempt at a generalized scheme was created based on a real space grid approach. The code breaks up the entire multi-atom system into subregions of space delineated by dividing the total occupied volume by an integer of equally spaced planes in each dimension. The spatial boxes are then interpreted as fragments. If the fragment size is too small or too large, the number of real space partitions can be adjusted. One disadvantage of this scheme is that chemically bound elements might be in adjacent boxes where it would make the most sense to keep them within the same fragment. Once an initial fragment is chosen, the system tests to see that atoms within a chosen effective bonding radius are added to the fragment. This is a slow algorithm that involves N^2 calculations where N is the number of atoms. The effective bonding radius is varied to achieve the desired average fragment size.

The total energy of the system within the DnC scheme is the trace over the product of density matrix (DM) and Fock matrix (FM) for the system. In the DnC scheme, the DM is block diagonal and the global trace can be written as a sum over fragment buffer traces:

$$E_{tot} = \mathrm{Tr}\left(\mathbf{DF}\right) \approx \sum_{I=fragments} \mathrm{Tr}\left(\mathbf{D}_I\mathbf{F}_I\right). \tag{2.1}$$

The fragment density matrix is obtained by diagonalizing the portion of the FM that is supported in the chosen fragment-buffer block and populating the resulting orbitals according to an effective finite temperature weight function. The fragment-buffers contribute to the global density matrix through

$$\mathbf{D}_I = \rho_{ij}^I \alpha_{ij}^I \tag{2.2}$$

where

$$\rho_{ij}^I = 2\sum_m f_\beta\left(\varepsilon_F - \varepsilon_m^I\right) C_{i,m}^{I*} C_{j,m}^I \tag{2.3}$$

is the density matrix as calculated and constructed within the I-th buffer-fragment region. ε_m^I is the eigenvalue of the m-th KS orbital calculated for the I-th fragment-buffer system. $C_{k,m}^I$ is a coefficient of the eigenvector of the m-th KS orbital on a basis function calculated for the I-th fragment-buffer system. ε_F is the global Fermi energy determined to ensure that the full system has the proper total number of electrons. f_β is the Fermi distribution function at effective inverse temperature β where α^I is a weight function chosen to be

$$\alpha_{ij}^I = \begin{cases} 1 & \text{if i and j basis functions are both centered on fragment atoms,} \\ \frac{1}{2} & \text{if either i or j basis function is centered on a fragment atom.} \end{cases} \tag{2.4}$$

The divide and conquer algorithm starts by the selection of fragments, sets of spatially proximate atoms that are likely to have significant chemical bonding. Once fragments are chosen, the buffer regions are selected by determining which adjacent fragments are likely to affect the electronic structure of the fragment in question. The buffers and fragments must be redetermined for every reconfiguration of atomic nuclei. The self-consistency cycle starts after the fragments and buffers are passed to the subsystem code. Each fragment buffer system is run as an independent single iteration calculation. From this calculation, the density matrix and eigenvalues is obtained. The fragment density matrices can be assembled into the global DM, and the trace of this object must be the total number of electrons. An internal loop varies the chemical potential for the entire system until the correct number of electrons is described. The resulting global density matrix is then used to recalculate the global Fock matrix. The entire process is repeated until self-consistent. The resulting density matrix can then be used to calculate the final energy.

Additionally, the forces can be calculated numerically for each atom using results of multiple full system DnC calculations through

$$F_{i,x} = \left(E\left(x_0 + \Delta_{i,x}\right) - E\left(x_0\right)\right)/\Delta_{i,x} \tag{2.5}$$

where x_0 denotes and reference configuration of atomic positions and Δ is a small displacement of on of the positions of one of the atoms determining a component of force on that atom. The force calculations can be performed for each atom and spatial direction separately leading to additional scaling linear in the number of atoms.

Our implementation is for finite systems. Approximations to phonons can be related to the restoring forces each atom exhibits. The restoring frequency of vibration for each atom can be calculated by perturbing the structure from equilibrium and using finite energy differences over displacements assuming a harmonic confinement. In a stable configuration of atoms, the force on each atom vanishes. Slight perturbations about this configuration result in harmonic motion of the nuclei with a frequency that can also be determined from total energy calculations. Information about the vibrational frequencies can be used to determine the phononic spectrum once all modes are known. The accurate and fast calculation of forces is important in the description of reactions of energetic materials.

This implementation described in this report uses MINDO3, a semi-empirical quantum mechanical method chosen here for its simplicity and speed [27, 28, 29]. More accurate density functional methods can be used instead, but this is not available in the current implementation. Generalization to DFT method follows straightforwardly and is currently being tested.

Chapter 3

Challenges

There are four major difficulties to establishing a robust linear scaling divide and conquer (DnC) calculation capability. These are the choice of fragments, the assignment of buffers, self-consistency problems, and the calculation of the Fock matrix.

The first is the assignment of fragments, distinct sets of atoms, in which the full quantum mechanic problem is solved. The determination of these units is mostly arbitrary but must be strongly guided by the relevant chemistry of the chemical system. The general method used to select fragments starts by calculating the volume of the entire many atom system. Then, the volume is subdivided into spatially local groups. The spatial local groups are tested to determine if they are bound to nearest neighbor groups, and if so, the original groups can be combined. Determination of whether to combine the groups depends on the average desired fragment size and the length of the chemical bonds when detected. The cut-off criteria and subdivision of the entire volume are adjusted until the desired average number of atoms per fragment is achieved.

Our performance runs used a modified scheme for CL20. The six atom fragments are assembled by first finding all the nitrogen-nitrogen (N-N) bonds in the CL20 molecule. This is done by starting with one N atom then searching for the nearest other N atom to it. Once an N-N bond is found those two atoms are removed from the pool of N atoms and the search moves to the next N atom to find its nearest N atom to form a bond. Once all the N-N bonds are found it then the code finds the nearest carbon (C) atom to form a C-N-N molecule the same way it found the N-N bonds. This is then repeated for the hydrogen (H) and 2 oxygen (O) atoms to form $H\text{-}C\text{-}N_2\text{-}O_2$ fragments. Once the fragments are chosen, the code generates the buffers. The fragment selection method was constructed to insure that all fragments are the same unit size, and the code checks so that atoms are not included twice. Once the atoms are added to a fragment they are removed from the atom pool to avoid picking atoms multiple times. The goal is to create a method that gave the user more control and accelerated the process. The general method is slow for larger systems such as the 1152 atom system. The convergence and results of a calculation depend on the judicious choice of fragments. In our implementation we have chosen to pick fragments with on average 6-8 atoms. The even number of atoms is chosen to keep an even number of electrons in the fragments. And units of 6-8 are comparable to what was successful for polymers. The actual numeric process of picking out fragments goes as the number of atoms squared and thus violates linear scaling. Considerable development is required here to implement the identification of fragments at a better scaling and with more built-in chemical intuition. The challenge of determining fragments was already discussed to some extent in the methods section of this document.

The next challenge is to determine the buffer regions. The buffer determines the boundary conditions on each fragment calculation by accounting for the surrounding region of space. Currently, any other fragment within a certain radius of any atom in the fragment is determined to be in the buffer region. The matching of fragments to buffers is also on the order of the number of fragments squared. A different scheme must be developed to reduce this scaling. Typically 2-3 buffers in each dimension is sufficient to converge the energies and forces in our trials. Perhaps a more judicious choice of fragments could allow a smaller number of buffers. The actual diagonalization of the global Fock matrix is of the fragment plus buffer blocks and thus reducing the size of the combined system greatly speeds the calculation.

The third challenge is the self-consistency of the density matrix. The DnC method is typically run repeatedly with the Fock matrix calculated from the density matrix of the previous cycle until a chosen system measurable, typically, the total energy, ceases to change between iterations within a tolerance. However, the effective global density matrix recreated from the density matrices of the fragments is prone to self-consistency issues. To a large extent this problem can be ameliorated by raising the effective temperature; however, the required temperatures are often several thousand Kelvin and much higher than desirable. An alternative would be to used mixing schemes akin to those used in all-electron quantum mechanical calculations to avoid oscillations in the SCF process. Unfortunately, simple mixing schemes do not help much. Work needs to be done to address specifically where the instability is arising, and a new method is likely needed to facilitate convergence in general.

The fourth challenge is the calculation of the Fock matrix. This too involves N^2 operations because of the Coulomb solve required. In our calculations, we explicitly calculate the full Fock matrix from the reassembled full density matrix. The path to improvement here is by using fast multi-pole solvers to accelerate the calculation of the Hartree and other Coulomb terms. Note that in a first principle implementation, the exchange and correlation terms are semi-local and only the Hartree term posses this challenge.

Chapter 4

Results

In this section, we illustrate how the divide and conquer (DnC) method can provide energies, forces, and harmonics in excellent agreement with all electron calculations for several ideal polymer systems and for some models of the high explosive CL20. In addition to the typical parameters required for a quantum mechanical simulation, there are three additional parameters specific to DnC, the size of the fragments themselves, the size of the buffer regions, and the effective temperature. We have chosen to focus principally on the size of buffer regions. Typical fragments are assumed to be on the order of 6-8 atoms. This is the size used successfully in earlier work on polymers. The number of atoms in the buffer regions is highly dependent on the effective local dimensionality of the problem. For example, it is found that linear polymers, which are effectively 1D, are typically well converged at buffers of about 4 times the number of atoms in the fragment. For 3D systems such as unreacted CL20, this total can be 4 times larger requiring 16 times the number of atoms of the fragment.

As an initial test, we validated the method against ideal models of polymers that have previously been studied with DnC. These ideal polymers are constructed as perfect linear chains with a discrete number of monomers each identified as a fragment. Figures 4.1 and 4.3 shown the geometry for 10 and 20 monomer chains of polyacetylene. The bond distances are set at approximate distances based on default settings in the molecular builder. Thus, these are not optimized geometries and will provide a good test for both energies and forces. The energies and forces are shown to converge for PA10 in Figure 4.2. Because large portions of the total energy and forces are the same in DnC and a full calculation, we use normalized units defined as the DnC result less the exact limit divided by the exact limit. Good convergence in terms of energy is already seen with buffer sizes of one monomer while forces require 2-3 monomers.

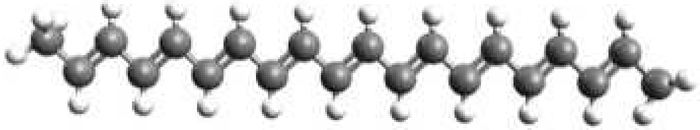

Figure 4.1. A idealized molecule of Polyacetylene-10 (PA10) used in this work.

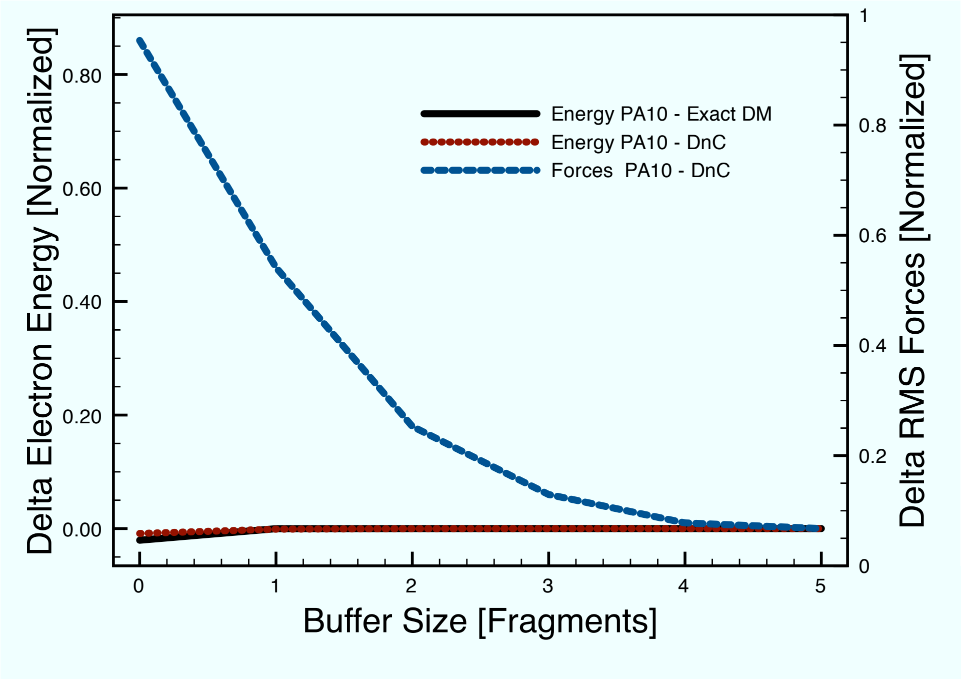

Figure 4.2. Convergence of total energy and forces with respect to the buffer size for PA10.

A similar trend is seen in Figure 4.4 where good convergence is achieved with buffers of 2-3 monomers. This is consistent with the DFT results found in earlier work on polypeptides by Yang [9, 10]. The curves in Figure 4.4 do not continue past 3 repeat units. This is because the current implementation limits in the total number of atoms allowed in the buffer-fragment regions to about 40 atoms due to requirements of the quantum mechanics solver called.

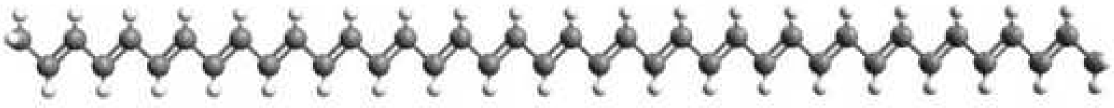

Figure 4.3. A idealized molecule of Polyacetylene-20 (PA20) used in this work.

The principal goal of these efforts is to improve simulations of reactive materials. Thus, it makes sense to test the implementation on a characteristic and relevant reactive material. CL20 is a nitroamine explosive also known as 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane and HNIW. It is primarily used in propellants but is being tested for stability and production capabilities for weapons potential. Because of an improved oxidizer-to-fuel ratio, it produces 20% more energy than traditional HMX-based propellants, and is often superior to other conventional

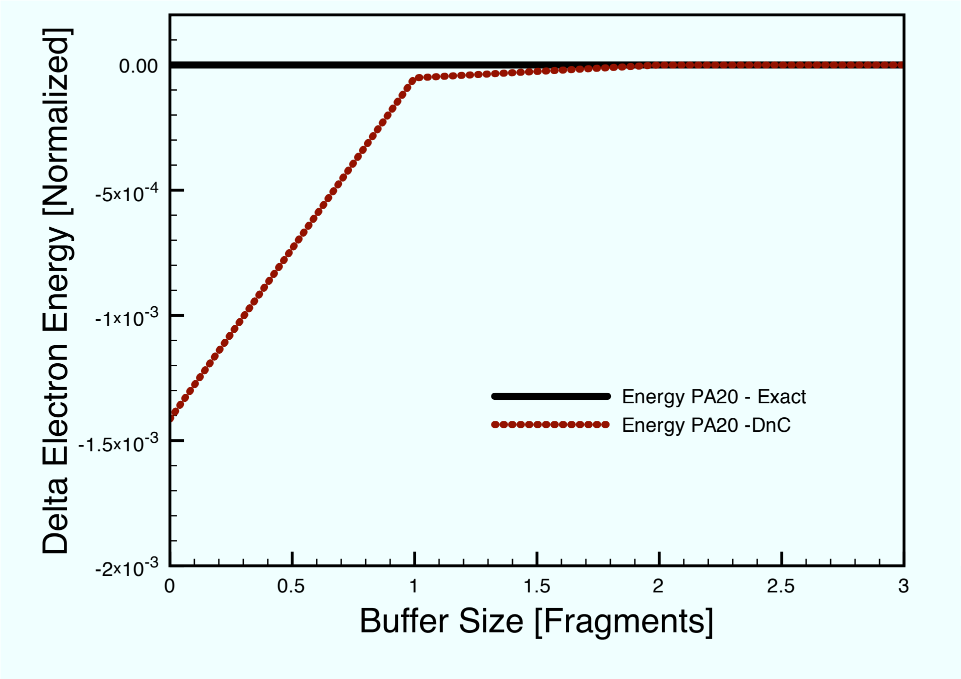

Figure 4.4. Convergence of total energy with respect to the buffer size for PA20.

high-energy propellants and explosives.

The designation CL20uc indicates that the simulation was performed on the system shown in Figure 4.5. In the simulations, fragments are chosen to maintain the integrity of the N-NO_2 units including carbons when needed. This structure (CL20uc) was optimized using periodic boundary conditions, but for the testing of the divide and conquer method it was considered as an isolated gas phase cluster. The forces on the atoms should be outward as the the periodic simulation is expected to slightly contract relative to the gas phase. Because the forces are non-vanishing, the unit cell provides a good test system for both energies.

Figure 4.6 shows the convergence of the energy and forces in scaled units as the number of buffers is increased. The fragments are roughly 6 atoms each. By a buffer size of 6 atoms, the forces and energy is well converged. It is important to note that while the absolute total error in forces is initially much larger for systems without buffers, the forces converge much faster than energy with the size of the buffer. This scales as the third power of the size of the buffer fragment systems. While some efficiency can be achieved by distributing the buffer-fragment system calculations among several processors, it is advantageous to use a buffer-fragment system with a size the maximizes the accuracy while balancing computational time per fragment.

The exact energy and force results are in non-standard units. The energy is the total energy of the entire system. It includes atomization energies and reference energies of the atoms. The total value is thus much larger than the relative energies typically used. For example, the total energy

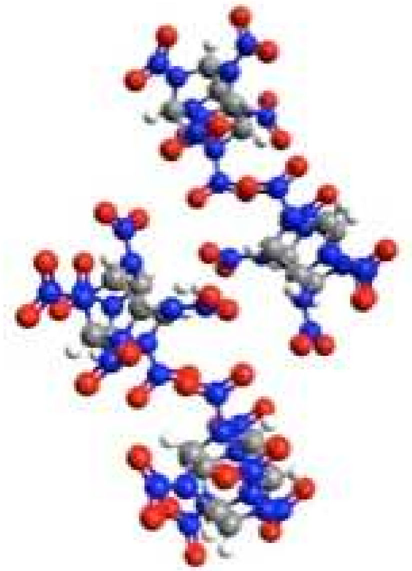

Figure 4.5. A unit cell of CL20 contains four molecules. It is treated in the gas phase as an isolated cluster in this work.

of the electrons in a carbon atom is about 0.6 keV, much larger than the eV energy scale of the valence electrons. Additionally, the ion-ion energy is included in the exact total. The forces are calculated within the energy units chosen over angstroms.

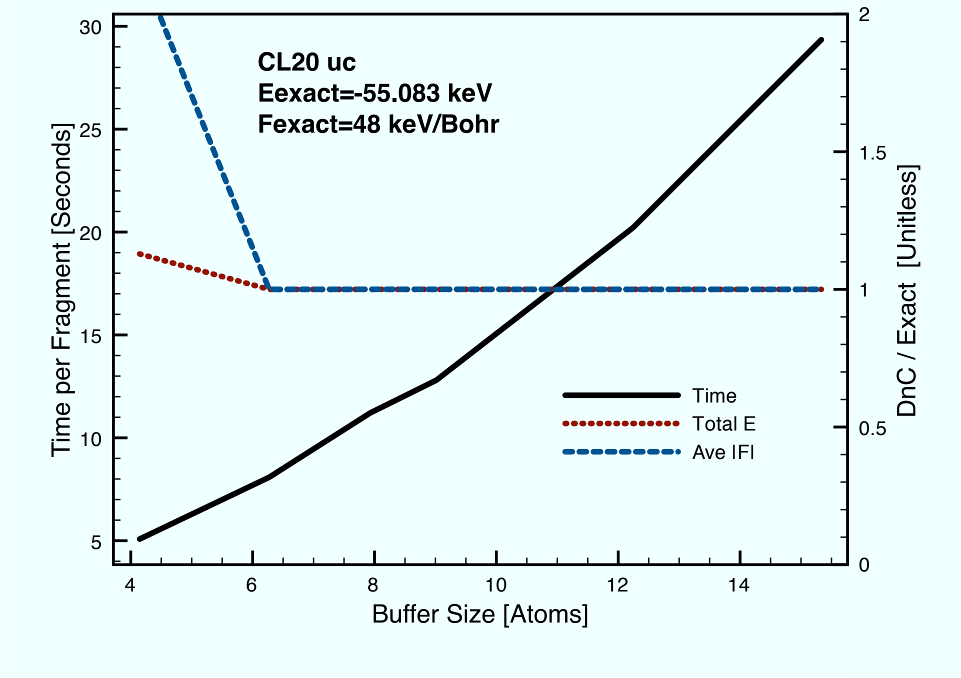

Figure 4.6. Convergence of energy and forces with respect to the buffer size for an isolated unit cell of crystalline CL20 with 144 atoms.

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Chapter 5

Conclusion

The divide and conquer (DnC) method is a promising scheme to allow quantum mechanics based calculations on systems with millions of atoms. This method is an improvement over existing force field methods because it systematically includes bond forming and breaking in simulations. We have implemented and tested a parallel version of the TLCC clusters demonstrating that DnC is capable of providing reliably accurate results for systems of interest: plastics, foams, and explosives. However, considerable work remains to make this scheme a reliable workhorse for predictive modeling of large systems. The current implementation works as expected on *clean* systems where the fragments and buffers can be chosen based on chemical intuition or by algorithm when there is a fortuitous positioning of the atoms. In the self-consistency cycle, the user must often tweak the cycle parameters to achieve convergence. The individual calculations can be greatly accelerated by using more efficient solvers. Major developments in the algorithm to select fragments and their buffers will be required, and the implementation of a fast multi-pole solver in determining the Fock matrix is desired. It is possible that even with these developments convergence will remain an issue. We recommend further exploration of this method at Sandia first focusing of the numerical selection of fragments and buffers.

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